Supplementary Information

Guided-formation of favorable interface for stabilizing Na metal solid-state batteries

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**Figure S1.** (a) Crystal structure of the as-prepared NZSP, (b) XRD pattern of NZSP with Rietveld refinement.
Figure S2 (a) EIS of NZSP pellets at low temperature from 25-80 °C, (b) Arrhenius plot of the NZSP ionic conductivity. The activation energy of the NZSP is 0.31 eV.
Figure S3 DC polarization and derived electronic conductivity of NZSP.
Figure S4. Comparison of the wetting behavior of NZSP and TiO$_2$-NZSP. Melted Na on top of the NZSP and TiO$_2$-NZSP surface show the classical wetting behaviors under different heating temperatures.

The wetting of liquid sodium on ceramic NZSP substrate shows a super-lithiophobic (defined as contact angle larger than 120º) behavior at 200 ºC in argon glove box.$^{[1]}$ That is because the interaction strength between Na-Na in Na structure is higher than that of interaction between Na with NZSP. Moreover, these two materials (metallic Na and ceramic NZSP) are very different in physico-chemical properties and electronic structures. The nature of the bonding between metallic Na and NZSP can be
discussed and analyzed by using an electronic approach. The NZSP has a high Na ion conductivity ($5.3 \times 10^{-4}$ S/cm at 25 °C, Figure 1, manuscript) and very low electronic conductivity ($0.8 \times 10^{-9}$ S cm$^{-1}$, Figure S3 ESI†). According to recent work of mine, NZSP surface could be comprised of oxygen anions, due to the polarization of the larger size oxygen anions and Na deficiency. When the liquid Na approaches the NZSP surface, the valence electrons of the metallic Na atoms will interact repulsively with the negative charges of many oxygen anions present on the NZSP surface. Consequently, the interactions between the metallic Na atoms and the NZSP surface are essentially physical (van der Waals) interactions at absolute zero.$^{[2]}$ When we increase the heating temperature, several electrons from the fully filled valence band of NZSP can pass through the bandgap into the conduction band by the thermal excitation effect, thus leading to the formation of holes in the valence band and free electrons in the conduction band. Then, the metallic Na atoms can interact chemically with the negatively charged oxygen anions on present on the NZSP surface structure. This also means that the surface structure of the NZSP can be stabilized by its contact with the metallic Na. Moreover, it is noted that the Na-O bond formed at the interface after the electron transfer at the Na-NZSP interface.
Figure S5. EIS results of the symmetric cells at room temperature. (a) Na/NZSP/Na, (b) Na/TiO$_2$-NZSP-TiO$_2$/Na.
Figure S6. EIS of Na/TiO$_2$-NZSP-TiO$_2$/Na of the symmetric cells at different aging times, 1 h, 10 h, 30 h, and 100 h.

As shown in Fig. S6, EIS of Na/TiO$_2$-NZSP-TiO$_2$/Na of the symmetric cells after 100 hours aging indicates that an interphase is formed and the reactions is likely to be diffusion-controlled.
**Figure S7.** Galvanostatic cycling of Na/TiO$_2$-NZSP-TiO$_2$/Na symmetric cell with a constant current density of 0.2 mA cm$^{-2}$.

When the NZSP-TiO$_2$ contact with metallic Na, a charge layer was formed due to the electrons and Na ions diffusion at the interface, which is one of the main factors affecting overpotential during charge/discharge at initial cycles. Afterward, the passivation layer on TiO$_2$ surface is formed, which is corresponds to the Na ion insertion.$^{[3]}$ As shown in Figure S7 (ESI†), the polarization potential was raised to about 0.2 V during the initial several cycles, which is corresponding to 0.84 Na$^+$ per TiO$_2$ based on the Ti$^{4+}$/Ti$^{3+}$ redox couple.$^{[4]}$ After formation of the interphase, the polarization potential decreased and stabilized to about 40 mV (0.2 mA cm$^{-2}$). Another higher overpotential of 60 mV is found around the 500th cycle during charge/discharge, which is possibly due to a phase transition between an amorphous anatase-like Na$_x$TiO$_2$ phase and disordered layered-like Na$_x$TiO$_2$ phase.$^{[5]}$ It has been confirmed by the TEM and selected-area electron diffraction (SAED), as shown in Figure 4h (in manuscript) and Figure S14 (ESI†). No matter which kind of structure of Na$_x$TiO$_2$ formed at different electrochemical conditions, they are all good Na ion conductors.$^{[6]}$

In summary, we introduce the TiO$_2$ film to guide a favorable Na$_x$TiO$_2$ interphase through an electrochemical activation for stabilizing the NZSP/Na interface.
Figure S8. DFT calculations of binding energy between Na metal and NZSP, TiO\textsubscript{2}-NZSP, and NaTiO\textsubscript{2}-NZSP interface, respectively. (a) Optimized structures of the NZSP/Na interface, (b) Optimized structures of the TiO\textsubscript{2}/Na interface, (c) Optimized structures of the NaTiO\textsubscript{2}/Na interface. Table S1, binding energies of NZSP/Na, TiO\textsubscript{2}/Na, and NaTiO\textsubscript{2}/Na calculated by DFT.
Figure S9. Scheme of the Darmstadt Integrated System for Battery (DAISY-BAT) integrated system showing the different deposition chambers which are connected via an UHV transfer system to the XPS/UPS analysis unit.\textsuperscript{[7]}
Figure S10. The comparison of C 1s peaks in XPS results for NZSP before and after heating treatment (Ar+O₂ 450 °C). It demonstrates that the carbide absorbed on the surface of NZSP can be removed by heating treatment.
Figure S11. XPS of O 1s (a), Si 2p (b) and P 2p (c) regions for the stepwise deposition of Na on the surface of NZSP solid-state electrolyte.
Figure S12. XPS valence band changes of the TiO$_2$-NZSP during stepwise Na deposition.
Figure S13. TEM image of the Na/Na$_x$TiO$_2$/NZSP interface. The sample was treated by FIB before the TEM observation.
Figure S14. Selected area electron diffraction of the ALD TiO$_2$ layer before and after deposition of metallic Na.
Figure S15. XPS of Ti 2p region for the stepwise adsorption of metallic Na on the surface of TiO$_2$-NZSP.
Figure S16. XPS of Zr 3d region for the stepwise adsorption of metallic Na on the surface of TiO$_2$-NZSP.
**Figure S17.** The Zr 3d, Ti 2p and valence band spectra of the NZSP, NZSP/Na$_x$TiO$_2$ interface, and Na$_x$TiO$_2$ film formed after metallic Na deposition experiments.
Figure S18. (a) The galvanostatic charge and discharge profiles of the NVP/NZSP/Na full cells at 0.1 C, 60 °C. (b) Capacity retention and cycling efficiency of the NVP/NZSP/Na full cells at 0.1 C, 60 °C.
Reference


